SYMPOSIUM Y

Solid Freeform and Additive Fabrication III

April 24 – 26, 2000

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* Invited paper

SESSION Y1: DIRECT METAL FABRICATION
Chairs: Paul F. Jacobs and Fritz B. Prinz
Monday Morning, April 24, 2000
Salon 13 (Marriott)

8:30 AM Y1.1
FABRICATION OF Ti-Al ALLOYS FROM ELEMENTAL POWDER BLENDS WITH THE LENS^{TM} TECHNOLOGY. Katrin I. Schwendner and Hamish L. Fraser, Dept. of Materials Science and Engineering, The Ohio State University, Columbus, OH.

Unlike conventional metalworking technologies, the LENS^{TM} process builds components in an additive manner. It is a direct material fabrication process in which a fully dense part can be formed. In the process a Nd:YAG laser is used to fuse metal powder into a solid component. To build parts from complex alloys such as Ti-Al alloys, powders with the desired composition have to be consolidated first. Generally the fabrication of these pre-alloyed powders is cost intensive. Therefore the use of elemental powder blends has been investigated. Samples with the following compositions have been deposited using elemental powder blends: Ti-10%Nb, Ti-10%Cr and Ti-48%Al-2%Cr-2%Nb. The influence of the various factors affecting the quality of these deposits will be discussed. The elemental blend deposits of Ti-48%Al-2%Cr-2%Nb have been compared with deposits form pre-alloyed powder. The deposit microstructures have been characterized using SEM and TEM techniques, and the role of microstructure will be discussed. After the deposition the Ti-48%Al-2%Cr- 2%Nb deposits show evidence of cracking. To avoid this stress relief heat treatments as well as the heating of the substrate prior to deposition have been investigated.

8:45 AM Y1.2
HEAT TREATMENT, MICROGRAPHIC EXAMINATION, AND THERMAL MODELING OF LASER FORMED Ti-6Al-4V. S.M. Kelly, S.L. Kampe, Virginia Tech Materials Science and Engineering Dept, Blacksburg, VA; C.R. Crowe, Virginia Tech Alexandria Research Inst., Alexandria, VA; K.T. Slattery, Boeing-Phantom Works, St. Louis, MO.

Ti-6Al-4V structural parts have been formed using a laser direct metal deposition process, known as laser forming. The laser forming process combines high power laser cladding technologies, with the advanced methodologies of rapid prototyping to manufacture complex, near-net shape metal parts. A large information base exists for heat treatments of forged and cast Ti-6Al-4V; however, there is presently not much information available on the heat treatment of laser formed Ti-6Al-4V. The work to be discussed is an investigation of the effect of heat treatment and cooling rates on the microstructure of bulk laser formed Ti-6Al-4V. The current results of a finite element model of the laser forming process will also be presented. The model will be used to relate the laser forming cooling rate and the observed microstructure of the as-formed samples with the cooling rate and microstructure obtained by conventional heat treatments.
The above research is sponsored by the Office of Naval Research.

9:00 AM *Y1.3
UNDERSTANDING THE MICROSTRUCTURE AND PROPERTIES OF COMPONENTS FABRICATED BY LASER ENGINEERED NET SHAPING (LENS). Michelle Griffith, Joseph Puskar, Charles Robino, Sandia National Laboratories, Albuquerque, NM; John Brooks, John Smugeresky, Sandia National Laboratories, Livermore, CA.

Solid freeform fabrication is one of the fastest growing automated manufacturing technologies that has significantly impacted the length of time between initial concept and actual part fabrication. This talk will describe recent developments in a new technology, known as LENS (Laser Engineered Net Shaping), to fabricate metal components directly from CAD solid models. In a manner analogous to stereo-lithography or selective sintering, the LENS process builds metal parts line by line and layer by layer. Metal particles are injected into a laser beam, where they are melted and deposited onto a substrate as a miniature weld pool. The trace of the laser beam on the substrate is driven by the definition of CAD models until the desired net-shaped densified metal component is produced. Direct fabrication of metals through LENS processing can enhance mechanical properties over those observed in conventionally processed materials. In 316 stainless steel, the yield stress can be doubled with no loss in ductility. We will describe our results with other materials (tool steel, titanium) to demonstrate our understanding of the connection between processing parameters (laser power, scan velocity, powder feed rate) and final material characteristics. We will show recent developments in our effort to determine to what extent the microstructure and properties could be predicted and controlled when using the LENS process. Finally, we will show applications of the technology.
This work supported by the U.S. Dept of Energy under contract DE-AC04-94AL85000. Sandia is a multiprogram lab operated by Sandia Corp., a Lockheed Martin Co., for the U.S. Dept of Energy.

9:30 AM Y1.4
CHANGES IN MICROSTRUCTURE AND MECHANICAL PROPERTIES OF STAINLESS STEEL 314S DURING SELECTIVE LASER SINTERING. Carl Hauser, T.H.C. Childs, K.W. Dalgarno, R.B. Eane, School of Mechanical Engineering, The University of Leeds, UNITED KINGDOM.

Four batches of stainless steel 314S powder with particle size fractions of -300+150 μm, -150+75 μm, -75+38 μm and -38 μm have been independently Selective Laser Sintered (SLS) within an argon atmosphere using a CO2 laser. Both single line passes and single layers were sintered then sectioned and prepared for metallographic inspection. Microstructural observations showed that increases in net heat input into the powder enlarged the melt volume fraction under the travelling laser beam causing grain coarsening and a change from a final solidified dendritic microstructure to a more prominent columnar microstructure. Mechanical tests were also carried out revealing property homogenisation of single layers as laser power increased and scan speed and scan spacing decreased. This paper maps the variations in microstructure and physical properties as scanning conditions change and highlights observations of melt pool quality variation within these conditions.

9:45 AM Y1.5
MICROSTRUCTURE AND PROPERTIES OF LASER DEPOSITED 304L AUSTENITIC STAINLESS STEEL. J.A. Brooks*, C.V. Robino**, T.J. Headley**, S.H. Goods*. *Sandia National Laboratories, Livermore, CA, **Sandia National Laboratories, Albuquerque, NM.

The use of laser deposition of powders to build three-dimensional structures is in many ways similar to a number of welding processes. It is well known that the solidification behavior and microstructures of 304L welds are highly dependent upon weld process and alloy composition. A wide range of microstructures from single-phase austenite to ferrite-austenite two-phase structures can be achieved. The goal of this work is to determine to what extent laser deposited austenitic microstructures could be obtained through the manipulation of composition, solidification mode, and solid state transformations. Samples of four different alloy compositions were deposited over a range of processing parameters that could yield fully dense structures. Microstructures of deposits were characterized using both optical and electron microscopy techniques and compared to those obtained during high energy density welding and to microstructural predictions. Tensile properties of the laser deposited structures will also be reported.
This work was funded by the Unites States Department of Energy under contract #DE-AC04-94AL85000.

10:30 AM Y1.6
A COMPARISON OF RESIDUAL STRESS CONTROL ISSUES FOR THERMAL DEPOSITION OF POLYMERS AND METALS IN SFF PROCESSES. Jack Beuth, Raymond Ong, Carnegie Mellon Univ., Dept. of Mechanical Engineering, Pittsburgh, PA; Nathan Klingbeil, Wright State Univ., Dept. of Mechanical & Materials Engineering, Dayton, OH; Lee Weiss, Carnegie Mellon Univ., Robotics Institute, Pittsburgh, PA.

Residual stress-induced tolerance loss is a significant concern in nearly all solid freeform fabrication (SFF) processes. Controlling residual stress-induced warping and other tolerance losses is essential in transitioning SFF processes from rapid prototyping applications to their use as functional prototyping or rapid manufacturing techniques. In this research, warping experiments and residual stress models are used to compare how residual stresses evolve in the building of metal and polymeric parts by thermal deposition-based SFF processes. Specifically, results for deposition of 304 stainless steel via a welding-based method are compared with results for deposition of ABS via an extrusion-based method. Both deposition methods are used in conjunction with CNC machining in the Shape Deposition Manufacturing process. Issues considered include the depth to which stresses are induced in existing material layers, the role of induced heating by the process in reducing residual stresses, the importance of high-temperature properties in determining final residual stress magnitudes and the directionality of warping for a raster-type deposition path. Each of these issues is considered with regard to strategies for reducing residual stress magnitudes (and warping) for both types of material systems.

10:45 AM Y1.7
NOVEL MICROSTRUCTURES BY DIRECT METAL DEPOSITION. Katherine C. Chen, California Polytechnic State University, Materials Engineering Dept., San Luis Obispo, CA; Dan J. Thoma, Los Alamos National Laboratory, Los Alamos, NM.

With the advance of solid freeform fabrication techniques, truly unique microstructures can be tailored for enhanced properties. Direct metal deposition allows rapidly solidified bulk samples to be produced in the near net-shape form. With cooling rates up to 10^5 K/s, metastable phases become possibilities. Microsegregation profiles at the liquid/solid interface indicate that interfacial equilibrium conditions are not necessarily adhered. Characterization of the rapid solidification behavior and the implications related to properties of the fabricated materials will be discussed. Furthermore, systematic investigations of processing parameters are coupled with solidification modeling efforts in order to understand processing-structure-properties relationships of various materials. For instance, doubling of the laser traverse speed results in the reduction of the primary dendrite arm spacings by 15% in the Fe-25Ni model system. As a consequence, ultimate tensile strength and ductility increase. In eutectic systems, direct metal deposition is employed to vary eutectic spacings, as well as, to control the growth direction with subsequent passes during fabrication. Length scales and connectivity of individual phases in multi-component alloys are thus somewhat controlled, and unique properties result. Such design of micro- structures for optimized properties is unattainable with conventional processing techniques.

11:00 AM Y1.8
CHARACTERIZATION OF LASER DEPOSITED NIOBIUM AND MOLYBDENUM SILICIDES. C.A. Brice, K.I. Schwendner, S. Amancherla, H.L. Fraser, The Ohio State University, Department of Materials Science and Engineering, Columbus, OH; X.D. Zhang, Reynolds Aluminum Company, Richmond, VA.

Recent advances in solid freeform fabrication techniques have opened the door to new methods for producing materials that are difficult to process by conventional means. Molybdenum and niobium silicides have the potential for high temperature structural applications, however, their low room temperature toughness has inhibited their practical use. Introducing a continuous second phase can greatly enhance the mecanical properties of these materials at low temperatures. This paper describes a method of in-situ alloying of molybdenum and niobium silicides using the LENS (Laser Engineered Net Shaping) process. Elemental blends of niobium/silicon and molybdenum/silicon/boron were laser deposited and the resultant microstructures were evaluated by various analytical techniques. The results show that a homogeneous in-situ composite can be produced where the silicide phases are toughened by a continuous eutectic phase.

11:15 AM Y1.9
PROCESS MAPS FOR BUILDING THIN-WALLED STRUCTURES BY LASER-BASED SFF PROCESSES. Jack Beuth, Aditad Vasinonta, Carnegie Mellon Univ., Dept. of Mechanical Engineering, Pittsburgh, PA; Michelle Griffith, Sandia National Laboratories, Albuquerque, NM.

In solid freeform fabrication (SFF) processes involving thermal deposition, thermal control of the process is critical for obtaining consistent deposition conditions and in limiting residual stress-induced warping of parts. In this research, nondimensionalized plots (termed process maps) are developed from numerical models of laser-based material deposition of thin-walled structures that map out the effects of changes in laser power, deposition speed and part preheating on melt pool size and residual stress magnitudes. The principal application of this work is to the Laser Engineered Net Shaping (LENS) process under development at Sandia Laboratories; however, the approach taken is applicable to any solid freeform fabrication process involving a laser or other moving heat source. Process maps are being developed in parallel with thermal imaging experiments as a means for checking the numerical predictions of melt pool size and for identifying key experiments to be performed. The results of this research will provide a better understanding of the interactions between process parameters and could serve as the basis for an automated process control system.

11:30 AM Y1.10
INVESTIGATION INTO FREEFORM FABRICATION OF MULTI-MATERIAL PARTS BY 3D WELDING AND MILLING PROCESS. Yong-Ak Song, Sehyung Park, Korea Institute of Science and Technology KIST, CAD/CAM Center, Seoul, KOREA.

3D Welding and Milling developed at Korea Institute of Science and Technology KIST combines the conventional welding and milling process to exploit the advantages of the both processes. On the one hand, the additive method gives the possibility to create features which have been impossible to manufacture so far such as internal channels and multi-material systems. On the other side, the machining process gives a high accuracy and surface quality. In this paper, freeform fabrication of parts using two different materials during deposition is experimentally investigated. When depositing a layer, a conventional mild steel is used to fill the area and a different type of steel such as stainless steel is used to fill the boundary area. In this way, a part is created which consists of a soft material inside and a material of different characteristics on the outside. This method of using different materials can be also extremely useful when building conformal cooling channels. Copper or bronze can be applied around the channel to increase the thermal conductivity of steel molds. The results of using two different materials in freeform fabrication and the process problems such as different thermal expansion are discussed in the paper.

SESSION Y2: TOOLING AND PHOTO PROCESSING
Chairs: Jack L. Beuth and Michelle L. Griffith
Monday Afternoon, April 24, 2000
Salon 13 (Marriott)

1:30 PM Y2.1
DIMENSIONALLY ACCURATE MOLD INSERTS AND METAL COMPONENTS BY DIRECT METAL LASER SINTERING. Jan-Erik Lind, Juha Kotila, Tatu Syvanen, Olli Nyrhila, Rapid Product Innovations Oy, Rusko, FINLAND.

One of the main shortcomings in the current rapid tooling techniques is the capability of producing only near net-shape parts. Direct Metal Laser Sintering (DMLS) is a technique that enables the fabrication of true net-shape parts in just a few hours and with only minimum post-processing. DMLS is a laser-based rapid tooling process developed in Europe by Electrolux Rapid Development Finland and EOS GmbH Germany. Electrolux Rapid Development was also the first to implement this technology to functional prototyping by using two proprietary bronze-based powders and a new steel-based powder. The technique enables the fabrication of tailored microstructures from porous matrix to near full density. Thus, functionally gradient structures can be fabricated, i.e. material is sintered to full density only where it is needed. This paper describes the philosophy of fabricating true net-shape mold inserts and metal components, but also concentrates on how to maintain the dimensional accuracy even after the post-processing. The study shows that even +/- 0.05 mm accuracy can be obtained. The results of the study also illustrate the beneficial effects of reduced layer thickness and post-processing on the surface roughness and mechanical properties as well as the suitability of various conventional and non-conventional coatings. With reduced layer thickness, the step-shaped effect of the layers was no longer visible. The surface was even further improved by shot peening and coating. In addition, case studies from injection molding, pressure die-casting and direct metal component fabrication are presented.

1:45 PM *Y2.2
ADVANCED MOLD DESIGN USING ADDITIVE FABRICATION. Paul F. Jacobs, Laser Fare Advanced Technology Group, Warwick, RI.

This paper will discuss recent developments involving the use of additive fabrication techniques in the design, development and fabrication of advanced core and cavity inserts currently being used in actual production injection molding applications. Starting with a CAD model of the part, one develops a CAD model of the tool, and then generates CNC cutter paths in order to machine a precision mandrel. Next, the active mold surface is developed in an additive process involving electroforming nickel directly onto the mandrel. After a sufficient thickness of nickel has been added to assure long tool life, the assembly is removed from the nickel vat and placed in a copper electroforming vat. A copper thermal management layer is then also fabricated through additive techniques. The electroformed copper layer is built until it fully encapsulates conformal cooling channels. Finally, the inserts are backed with steel, fitted with ejector pins, and secured in a steel mold frame. Finite element analysis mold temperature distributions will be shown for conventional machined steel inserts. These will be compared with temperature distributions for the new electroformed nickel-copper inserts backed with steel. Specifically, data will be presented regarding: (1) the use of high thermal conductivity mold materials, (2) the influence of conformal cooling channels, (3) active mold surface temperature distributions during injection molding, and (4) reductions in mold cycle time.

2:15 PM Y2.3
CONFORMAL COOLING VS. CONVENTIONAL COOLING: AN INJECTION MOLDING CASE STUDY WITH 3-DIMENSIONAL PRINTING. Wayde R. Schmidt, Ronald D. White*, Connie E. Bird and Joseph V. Bak, United Technologies Research Center, East Hartford, CT. *GE Appliances, Louisville, KY.

A series of designed experiments was performed in an attempt to quantify the historically "anecdotal" benefits of conformal cooling for injection molding tooling. The study considered different generic part geometries, gating schemes, mold materials and cooling approaches. This presentation will provide an overview of the mold design approach, cooling simulation, tool fabrication via the 3DPrinting(TM) process, as well as part molding and inspection results.

2:30 PM *Y2.4
RAPID ELECTROFORMING TOOLING. Bo Yang, New Jersey Institute of Technology, Department of Mechanical Engineering, Newark, NJ; Ming C. Leu, University of Missouri-Rolla, Department of Mechanical and Aerospace Engineering and Engineering Mechanics, Rolla, MO.

This paper presents an analytical and experimental study of a relatively new rapid tooling process called the Rapid Electroforming Tooling (RET) process. This process integrates solid freeform fabrication (SFF) with electroforming to produce molds, dies, and electric discharge machining (EDM) electrodes of intricate geometry rapidly and accurately. The basic process steps involved in RET are as follows. An SFF part is built and metalized for electroforming. The part is then placed in an electroplating solution and metal is deposited upon the part by electrolysis. When the desired thickness of metal has been deposited, the SFF part is separated from the metal shell, and the shell is backed with other materials to form a mold cavity or an EDM electrode. A nickel electroform can be used for a prototyping mold or even a production mold, and a copper electroform can be used as an EDM electrode. Thermomechanical finite element analysis implemented in ANSYS software was used to predict the thermal stresses generated during the burnout process that removes a stereolithography SFF pattern from the electroform. The thermal stress analysis was performed for stereolithography patterns of two- and three-dimensional geometry and varying electroform thickness. An experiment was conducted using strain gages to measure the thermal stresses induced during the pattern burnout process. The results of experiment agree well with the predicted thermal stresses.

3:30 PM Y2.5
DMD PROCESS PROVIDES UNIQUE MICROSTRUCTURES FOR IMPROVED STRENGTH AND DIE LIFE; ABILITY TO CREATE SMART PARTS. Dwight M. Morgan, Precision Optical Manufacturing Company, Plymouth, MI.

This presentation will review the benefits of direct metal deposition (DMD), with specific focus on materials used in solid freeform processes, the value of uniform grain size and the metallic blending capabilities resulting from this new technology. SFF processes, such as DMD, can improve part strength and die life, and give users the ability to create unique, functionally graded materials. DMD produces a unique microstructure with consistent grain size and very little variation in hardness. This improves property strength and can significantly improve the life of costly, 'mission critical' die casting tools. Tool steel alloys made by the DMD process do not present challenges seen with cast steel processes, where alloy additions in the ingots tend to separate from the melt due to slow cooling. This separation affects final mold/tool quality as properties like hardness cannot be consistently achieved. Instead of casting ingots, an all alloy tool steel tool or die is produced directly from tool steel in powder metal form. The rapid solidification of the process promotes almost no material separation. The alloy elements and carbides are finely distributed throughout the part. This results in isotropic properties and superior die performance. DMD also allows for the use of pure copper and aluminum. By using these highly conductive and reflective materials, multi-metallic inserts can be fabricated for high-wear, high-temperature and/or high-corrosion environments. This capability also lends itself well to the fabrication of functionally graded materials known as smart parts. Using DMD, powders can be blended to create alloys with unique physical properties, such as a tough innter core and high-strength, abrasion resistant outer surface. Lastly, DMD allows for the use of ceramics and metals to be fabricated in the same article. DMD is the first production process to allow for the direct fabrication of these "cermets", which have been employed in products that require unique thermal insulation, but also strength and ductility.

3:45 PM *Y2.6
SELECTIVE LASER SINTERING OF ZIRCONIA. Nicole Harlan, Seok-Min Park, David L. Bourell, J.J. Beaman, Jr., Mechanical Engineering Dept. and Texas Materials Institute, The University of Texas at Austin, Austin, TX.

A combination of Selective Laser Sintering and colloidal infiltration has been used to create partially stabilized zirconia molds for titanium casting. The mold material system was chosen for its low reactivity with molten titanium and thermal shock resistance. The base material, stabilized zirconia mixed with a copolymer binder, was pre-processed before laser sintering into the desired green shape. The average density of the fired parts could be increased to twice that of the green density. Hole sizes as small as 180 μm are possible in fully dense ceramic components.

4:15 PM Y2.7
PROCESSING-STRUCTURE-PROPERTY RELATIONS OF POLYMER-POLYMER COMPOSITES FORMED BY CRYOGENIC MECHANICAL ALLOYING FOR SELECTIVE LASER SINTERING APPLICATIONS. Jeffrey P. Schultz, Julie P. Martin, Ronald G. Kander, Carlos T.A. Suchicital, Virginia Tech, Department of Materials Science and Engineering, Blacksburg, VA.

Cryogenic mechanical alloying (CMA) has been shown to be an effective means for producing composite powders for selective laser sintering (SLS). Unlike composite particles made by a coating process, both phases are continuous throughout the particles formed by CMA. Consolidation of these composite particles via SLS offers the possibility of forming parts with a co-continuous microstructure. In this research, the microstructure of mechanically alloyed polymer-polymer composites for use in the SLS process is investigated using transmission electron microscopy. By varying the charge ratio and milling time of the CMA process, the phase domain size of the resulting composite powder can be manipulated and the physical and mechanical properties of the composite altered. This ongoing work explores the microstructural evolution as the composite powders are consolidated via SLS into macroscopic parts, as well as the relationships between microstructure and bulk properties.

4:30 PM Y2.8
FREEFORM FABRICATION OF FUNCTIONAL SILICON NITRIDE COMPONENTS BY DIRECT PHOTO SHAPING. Susanna Ventura, Subhash Narang, Philippe Guerit, Susan Liu, SRI International, Menlo Park, CA; Doug Twait, AlliedSignal Ceramic Components, Torrance, CA; Pramod Khandelwal, Rolls-Royce Allison, Indianapolis, IN.

SRI International has developed Direct Photo Shaping (DPS), a new low-cost multilayer freeform fabrication process. This paper describes DPS fabrication of functional silicon nitride gas turbine engine components. Visible digital light projection is used as a maskless tool to selectively photoexpose a photoactive ceramic dispersion. For each layer the projected image is changed according to the CAD data describing the object being built and solidification takes place by photocuring of the exposed areas. Multiple layers are dispensed and photocured to fabricate the object of interest. The resulting green ceramic part is then fired and sintered into a fully dense ceramic part. Silicon nitride vanes for a Rolls-Royce Allison industrial gas turbine were fabricated from AlliedSignal AS800 silicon nitride. A high quality surface finish was achieved with minimal finishing. The vanes were burner-rig tested under repeated thermal cycling with no distress to the component. Co-processed AS800 material was flexure-tested with excellent results. Hollow vanes of Rolls-Royce Allison's design are currently being built by DPS to facilitate cooling and allow a higher engine operating temperature. DPS has also been applied to the fabrication of alumina parts.

4:45 PM Y2.9
REFRIGERATIVE STEREOLITHOGRAPHY WITH DIRECT MASKING FOR SUPPORT-FREE AND ACCURATE FABRICATION. Tamotsu Murakami, Akiya Kamimura, Naomasa Nakajima, Univ of Tokyo, Dept of Engineering Synthesis, Tokyo, JAPAN.

The authors propose a new method named "refrigerative stereo-lithography". In its process, a liquid photopolymer resin for a new layer is supplied, cooled to become gel state, and then photopolymerized. After repeating this process for all layers, a photopolymerized object is fabricated in a gel resin block. The object can be obtained by heating the block, melting and removing only the non-photopolymerized resin. Using a gel layer, instead of a liquid layer as in conventional stereolithography, leads to some advantages. First, so-called "support" structures for isolated or overhanging shapes are unnecessary and distortion by photopolymerization might be reduced, because the object being fabricated is buried in and held by gel resin. Second, additional treatments for layers can easily be introduced. For example, excessive light exposure is needed in stereolithography to solidify the resin beyond one layer thickness, because the solidified layer must be firmly bonded to the previous layer. That can cause surplus growth by overcuring at the downward surfaces of the solidified object and leads to a dimensional error in the height direction. Suppose, however, we draw a mask only on the portion where surplus growth is unnecessary with a material which blocks light, supply new resin layer, and then photopolymerize it. By such treatment, height direction accuracy can be improved because the mask blocks the light exposure and avoids surplus growth only where it is unnecessary. Also, if we supply new gel resin layer and then draw a mask on its surface only where photopolymerization is unnecessary, we can solidify a required shape using a lamp instead of laser scan. Since we draw such mask directly on the gel resin layer, we name it "direct masking" method. The effectiveness of the refrigerative stereolithography with direct masking is confirmed by theory, simulation and experiment.

SESSION Y3/V3: JOINT SESSION:
DIRECT PATTERNING
Chairs: Duane Dimos and Douglas B. Chrisey
Tuesday Morning, April 25, 2000
Salon 12/13 (Marriott)

8:30 AM *Y3.1/V3.1

MATRIX ASSISTED PULSED LASER EVAPORATION DIRECT WRITE (MAPLE DW): A NEW METHOD TO RAPIDLY PROTOTYPE ACTIVE AND PASSIVE ELECTRONIC CIRCUIT ELEMENTS. D.B. Chrisey, A. Pique, J.M. Fitz-Gerald, R.C.Y. Auyeung, H.D. Wu, S. Lakeou and R. Chung, Naval Research Laboratory, Washington, DC.

We have developed a novel laser-based approach to do rapid prototyping of active and passive circuit elements called MAPLE DW. This technique is similar in its implementation to laser induced forward transfer (LIFT), but different in terms of the fundamental transfer mechanism and materials used. In MAPLE DW, a focussed pulsed laser beam interacts with a composite target on a laser transparent support or ribbon. Ideally, the laser energy causes the particulate and organic target material to be transferred to the substrate to form an adherent and conformal coating with minimal modification. Subsequent laser annealing, preferably in situ, is required to fully densify the coating and remove residual organic material. MAPLE DW is carried out at room temperature and atmospheric pressure and it has been demonstrated to work with many different classes of materials (e.g., metals, dielectrics, ferro-electrics, ferrites, polymers, and organics) and to $<$10-micron resolution. The final properties of the materials deposited depend on the deposition conditions and materials used, but when optimized, the properties are competitive with other comparable rapid prototyping techniques. Also, because the firing of the laser and the workpiece and substrate motion is computer automated, this technique is CAD/CAM compatible. A survey of the prototype devices fabricated by MAPLE DW, as well as a comprehensive description of the transfer mechanism, will be given.

9:00 AM Y3.2/V3.2

PATTERN WRITING BY IMPLANTATION IN A LARGE-SCALE PLASMA SOURCE IMMERSED ION IMPLANTATION SYSTEM WITH A PLANAR RFI PLAMSA SOURCE. Lingling Wu, Dennis M. Manos, College of William and Mary, Department of Applied Science, Williamsburg, VA.

A large-scale plasma source immersed ion implantation (PSII) system with planar coil RFI plasma source has been used to study an inkless, deposition-free, mask-based surface conversion patterning as an alternative to direct writing techniques on large-area substrates by implantation. The apparatus has a chamber 0.61m in diameter and 0.51m tall, with a base pressure in the 10^{-8}torr range, making it one of the largest available PSII systems. The system uses a 0.43m diameter planar rf antenna to produce dense plasmas capable of large-area, uniform materials treatment. The process causes minimal dimensional change, avoids thermal distortion of the written surface profiles and can treat nonplanar surfaces simultaneously without tilting or rotating. Metallic and semiconductor samples have been implanted with various plasma compositions to produce small geometric patterns of interest for device manufacturing. Samples are characterized by variable-angle spectrometric ellipsometry (VASE), SEM, AES, SIMS, and XPS, and for electrical and mechanical properties. Experimental depth profiles are in good agreement with Monte-Carlo calculations (Profile Code), showing layer-like nitrogen depth profile with implanted nitrogen concentration around the stoichiometry level. Measured linewidth and profiles are compared to the mask features to assess lateral diffusion, pattern transfer fidelity, and wall-effects. The paper presents the results of MC-hybrid and PIC calculations of the flux and angles of ion trajectories through the boundary layer. The uniformity of flux as a function of (3-D) location on targets is one output of these calculations. The calculation also modeled the sheath expansion and helped to assess the fidelity of pattern transfer as a function of feature size. The model calculations are also able to predict the uniformity of implanted dose within small features such as trenches and vias.

9:15 AM *Y3.3/V3.3

LASER AND FOCUSSED ION BEAM DIRECT-WRITE GROWTH OF 3-DIMENSIONAL MICRO- AND NANOSTRUCTURES. M. Stuke, K. Kahlke, K. Mueller, A. Schertel Max-Planck-Institut f. biophys. Chemie, Goettingen, GERMANY.

Three different regimes of direct-write growth will be discussed: (1) growth of ceramics from gas phase precursor mixtures including dimethylethylaminealane/oxygen and continuous wave/pulsed laser surface exposure in the visible resulting, with high growth rate, in complex three-dimensional aluminum oxide structures, which - if required - can be metallized with platinum using gas phase $Pt(PF_3)_4$, (2) metal growth from surface adsorbed precursors and pulsed UV laser exposure with short pulses, (3) growth of metals from surface adsorbed precursors including $W(CO)_6$ and focussed Ga ion beam exposure yielding tungsten structures with down to sub-100 nm precision. Examples and applications will be presented.

9:45 AM Y3.4/V3.4

INK-JET DEPOSITION OF CERAMIC SLURRIES. N. Reis, B. Derby, UMIST, Manchester Materials Science Centre, UNITED KINGDOM.

We have successfully printed green ceramic objects from slurries of Al_2O_3 dispersed in a paraffin wax using a commercial ink-jet printer developed for pattern making (Sanders Modelmaker 6-PRO). Ceramic suspensions are generally more viscous than the fluids normally passed through ink-jet heads. This may alter the response of the ink-jet printing system to its process parameters, e.g. driving voltage and frequency. We have explored the influence of fluid properties on ink-jet behaviour using CFD modelling and a parallel experimental study to determine the optimum ink-jet printing conditions for ceramic suspensions.

10:00 AM Y3.5/V3.5

LATERAL REDISTRIBUTION AND FILM PROFILES DURING INK-JET PRINTING OF POLYMER LED's. T.R. Hebner, B. Diamond, F. Pschenitzka, C. Madigan, X. Jiang, R. Register, S. Troian and J.C. Sturm, Center for Photonics and Optoelectronic Materials, Princeton University, Princeton, NJ.

The direct patterned deposition by ink-jet printing of polymers is an attractive option for forming patterned areas of thin polymer films with different light emitting properties (red, green, blue) for organic LED flat panel displays [1-2]. Conventional deposition techniques such as spin-coating lead to blanket films of a single color, and subsequent pattering of blanket films is difficult. For ink-jet printing of polymer LED's, one deposits a solvent droplet with the dissolved desired materials on an impermeable surface (e.g. indium tin oxide). The final profile of the deposited materials will critically depend on the redistribution of the dissolved molecules and polymers within the solvent droplet during the drying process. During drying, the liquid can flow within the droplet due to thermally-driven and convective-driven flows. In this paper, we examine the effect of such flows on the lateral distributions of organic dyes and small electron transport molecules in the final polymer film. When edge-pinning of the droplet occurs during drying, such flows can lead to a severe segregation of the dyes and molecules to the edge of the film, such that less than 1% of them remain in the active structure. This effect has been probed by photoluminescence and also by an X-ray microprobe. The effect can be overcome by reducing the driving force for the lateral segregation by reducing the deposition temperature of the droplets, or by chemically bonding the molecules to a polymer backbone. Both methods have been demonstrated successfully in LED's practice, which will be discussed.

1. T.R. Hebner and J.C. Sturm, Appl. Phys. Lett. vol. 73, 1775-1777 (1998).
2. S.-C. Chang, J. Bharathan, Y. Yang, R. Helgeson, F. Wudl, M.B. Ramey and J.R. Reynolds, Appl. Phys. Lett. vol. 73, 2561-2563 (1998).

10:30 AM Y3.6/V3.6

CALCULATION OF HAMAKER CONSTANTS IN NON-AQUEOUS FLUID MEDIA. Nelson S. Bell and Duane Dimos, Sandia National Laboratories, Albuquerque, NM.

Colloidal processing of materials is a necessary component of many new techniques for freeform solids fabrication. The design of a solid-liquid system for creating an optimal dispersion must balance the advantages and disadvantages of material solubility, solvent viscosity and solvent boiling point/vapor pressure. Information on the effect of solvent choice on the van der Waals interaction between materials in not readily available for many systems other than water. This talk will discuss the calculation of Hamaker constants from spectroscopic information available in the literature, present Hamaker constants for several nonaqueous systems, and give some experimental results regarding the choice of a fluid system on solid freeform deposition for sample materials in the electronics industry.

10:45 AM Y3.7/V3.7

NANOTECTONIC PRINTING: DIRECT PATTERNING OF NANOPARTICLE INKS TO FORM FUNCTIONAL LOGIC AND MICRO-ELECTRO-MECHANICAL SYSTEMS. Colin Bulthaup, Sawyer Fuller, Eric Wilhelm, Saul Griffith, Brent Ridley, Brian Hubert, Joseph Jacobson, MIT, Media Lab, Cambridge, MA.

Recently (Science, 286,746, October 22, 1999) we demonstrated an all-inorganic field effect transistor fabricated by printing. This was accomplished by developing a novel nanoparticle ink material and led to the highest mobility transistor which has yet been demonstrated by printing. The term nanotectonics refers to building functional structures(both logical and mechanical) from such nanoparticle inks. In this paper we report on recent progress towards directly patterning such nanoparticle inks to create both logic and machines (micro-electro- mechanical).

11:00 AM *Y3.8/V3.8
RAPID PROTYPING OF PATTERNED FUNCTIONAL NANO-STRUCTURES. C. Jeffrey Brinker, Hongyou Fan, Yunfeng Lu, Dhaval Doshi, Nicola Huesing and Gabriel P. Lopez, Univ of New Mexico, Sandia National Labs, Advanced Matls Lab, Albuquerque, NM.

Beginning with a dilute, homogeneous solution of ethanol, water, surfactant, and soluble silica, we recently demonstrated the rapid, continuous formation of ordered mesostructured films by dip-coating. Preferential evaporation of ethanol enriches the depositing film in surfactant, water and silica, inducing micellization and the formation of a variety of ordered silica/surfactant mesophases (hexagonal, cubic, lamellar). This presentation will first provide a brief overview of our evaporation-induced self-assembly (EISA) approach and its extension to the preparation of hybrid, organic-functionalized silica frameworks as well as metal-silica and (organic) polymer-silica nanocomposite films and particles. Then we will discuss new results where we utilize such homogeneous silica/surfactant solutions as inks in a variety of rapid prototyping processes like micropen lithography, ink-jet printing, and selective de-wetting. As previously demonstrated for dip-coating, evaporation accompanying these writing processes drives self-assembly into ordered mesophases. The resulting materials exhibit form and function on multiple length scales: on the molecular scale, functional organic moieties are positioned on pore surfaces, on the mesoscale, mono-sized pores are organized into 1-, 2-, or 3-dimensional networks, providing size-selective accessibility from the gas or liquid phase, and on the macroscale, 2-dimensional arrays and fluidic or photonic systems may be defined. Finally by introduction of photosensitive molecules into the inks, we can write arbitrary patterns of photosensitive mesophases. A subsequent lithographic patterning step then can be used to photo-define different functionalities within the parent pattern, providing an efficient route to hierarchically organized functional materials.

11:30 AM Y3.9/V3.9
RAPID FABRICATION OF PATTERNED FUNCTIONAL NANO-STRUCTURES VIA DIRECT WRITING AND PRINTING. Hongyou Fan, Yunfeng Lu, Scott T. Reed, Tom Baer, Randy Schunk, Gabriel P. Lopez and C. Jeffrey Brinker, The University of New Mexico/NSF Center for Micro-Engineered Materials, The Advanced Materials Laboratory, Sandia National Laboratories, Albuquerque, NM.

The ability to engineer ordered arrays of objects on multiple length scales has potential for applications such as microelectronics, sensors, wave guides, and photonic lattices with tunable band gaps. Since the invention of surfactant templated mesoporous sieves in 1992, great progress has been made in controlling different mesophases in the form of powders, particles, fibers, and films. To date, although there have been several reports of patterned mesostructures, materials prepared have been limited to metal oxides with no specific functionality. For many of the envisioned applications of hierarchical materials in micro-systems, sensors, waveguides, photonics, and electronics, it is necessary to define both form and function on several length scales. In addition, the patterning strategies utilized so far require hours or even days for completion. Such slow processes are inherently difficult to implement in commercial environments. We present a series of new methods of producing patterns within seconds. Combining sol-gel chemistry, Evaporation-Induced Self-Assembly (EISA), and rapid prototyping techniques like pen lithography, ink-jet printing, and dip-coating on micro-contact printed substrates, we form hierarchically organized silica structures that exhibit order and function on multiple scales: on the molecular scale, functional organic moieties are positioned on pore surfaces, on the mesoscale, mono-sized pores are organized into 1-, 2-, or 3-dimensional networks, providing size-selective accessibility from the gas or liquid phase, and on the macroscale, 2-dimensional arrays and fluidic or photonic systems may be defined. These rapid patterning techniques establish for the first time a link between computer-aided design and rapid processing of self-assembled nanostructures.

11:45 AM Y3.10/V3.10
ELECTROSTATIC PRINTING, A VERSATILE MANUFACTURING PROCESS FOR THE ELECTRONICS INDUSTRIES. Robert H. Detig, Electrox Corporation, Denville, NJ.

Functional materials configured as liquid toners are printed on a variety of substrates for various manu- facturing processes. The materials include metal toners, resistor toners, high k dielectric toners, phosphors and ITO. The substrates printed upon include glass, bare and coated metal, polymeric film and even paper. A fixed configuration electrostatic printing plate is used in most manufacturing applications though traditional photo receptor plates can be used if electronic addressibility is desired. Applications of electrostatic printing for electronic packaging products (printed wiring boards and flex circuits) and of passive electronic components themselves will be shown. Possible applications of toners to the manufacture of flat panel displays will be discussed. Results with a pure silver toner printed on both glass and paper will be reported. Examples of passive electronic components like resistors, capacitors, and even inductors that have been electrostatically printed with liquid toners will be shown.

SESSION Y4: COMPOSITES AND CERAMICS
Chairs: Paul Calvert and John W. Halloran
Tuesday Afternoon, April 25, 2000
Salon 13 (Marriott)

1:30 PM Y4.1
MODELING AND OPTIMIZATION OF NOVEL ACTUATORS PRODUCED BY SOLID FREEFORM FABRICATION. Bryan A. Cheeseman, Xiaoping Ruan, Tsu-Wei Chou, University of Delaware, Center for Composite Materials and Department of Mechanical Engineering, Newark, DE; Ahmad Safari, Stephen C. Danforth, Rutgers University, Department of Ceramic Science and Engineering and Center for Ceramic Research, Piscataway, NJ.

The ability of Solid Freeform Fabrication (SFF) to produce complex piezoceramic architectures has enabled the development of novel designs for PZT actuators. Recently, it has been shown that through the intelligent application of actuator geometry, poling direction, piezoelectric material direction and electric field, the force and displacement output of a PZT actuator could be optimized [1]. The current investigation examines several piezoceramic actuator geometries, including dome and spiral- shaped actuators and a telescoping-type actuator as shown in Figure 1. Using finite element analysis, parametric studies are performed to identify some key issues in the optimization of actuator performance. Parameters investigated include actuator height, thickness, length and piezoelectric property orientation. Results of the dome study indicate that an actuator having a tangentially alternating poling direction and applied electric field exhibits a much larger displacement and force response when compared to dome actuators having either a through-the-thickness or tangential poling direction. Analysis of spiral actuators indicates that the spiral geometry results in pronounced displacement amplification when compared to the displacement of an equivalent length piezoelectric strip. In summary, some remarks will be made on the optimal use of piezoelectric material properties and actuator geometry in actuator design.
[1] X.P. Ruan, et al. (1999). “Design Optimization of Dome Actuators.” *IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control*. **46.** *1-8*.

1:45 PM *Y4.2
PROCESSING OF ORGANIC/INORGANIC COMPOSITES BY STEREOLITHOGRAPHY. Jim H. Lee, Robert K. Prud'homme, and Ilhan Aksay, Princeton University, Princeton Materials Inst., Princeton, NJ.

Ceramic StereoLithography (CSL) is used to fabricate complex shape ceramic powder compacts by laser photocuring a concentrated ceramic dispersion in photocuring solutions layer-by-layer. The main processing parameters in CSL such as layer thickness, resolution, hatch spacing, and overcure depend on the knowledge of light propagation in concentrated multiple scattering dispersion. In studies dealing with the processing of ceramic-filled organics, we investigated the depth of curing for model resin systems as a function of photoinitiator concentration. An optimal photoinitiator concentration that maximized the gel cure depth was observed. Two regimes were shown to exist in which the swell ratio was minimized or maximized. The study showed that photoinitiator plays a significant role in controlling the quality and performance of the formed gel network, with special regard to thickness of cured layers. This has potential application to fields as diverse as industrially cured coatings and dental fillings, and more generally, 3-dimensional fabrication techniques.

2:15 PM Y4.3
FREEFORM FABRICATION OF BONE IMPLANTS MATERIALS COMBINING A STRONG SUPPORT MATERIAL WITH A BIODEGRADABLE COMPOSITE. Joe Walish, Ranji Vaidyanathan, Advanced Ceramics Research, Tucson, AZ; Shantha Sarangapani, ICET Inc. Norwood, MA; Haripin Chandra, Christian Harajanto and Paul Calvert, Department of Materials Science and Engineering, University of Arizona, Tucson, AZ.

There has long been interest in biodegradable prosthetic bone materials. An ideal material would be osteoinductive, promoting new bone formation. It would also be tough and carry load until it is wholly replaced by new bone. No existing material is wholly satisfactory. Ceramics and glasses tend to be too brittle for use in stressed sites. Biodegradable polymers tend to lose strength long before they lose mass and are replaced. Freeforming methods have been used to make porous implants from slowly-degradable polyesters. These are then impregnated with a biodegradable polyester/ hydroxyapatite blend. We will report on mechanical properties of these implants at different stages of degradation in vitro, on studies of degradation kinetics and on biocompatibility. In general, freeforming methods offer a powerful route to forming such multi-component biomedical materials.

2:30 PM Y4.4
BIOCERAMICS AND PIEZOELECTRIC SENSORS BY DIRECT AND INDIRECT INKJET DEPOSITION. Gabriel T-M. Chu, Chris J. Reilly, John W. Halloran, Department of Materials Science and Engineering; Scott J. Hollister, Departments of Biomedical Engineering, Surgery and Mechanical Engineering, University of Michigan, Ann Arbor, MI.

Indirect inkjet printing of ceramics is done using wax molds from a conventional 3D inkjet printing machine. Thermal-curable suspensions of ceramic powders in acrylates are cast into the molds, followed by curing, binder burnout and sintering. Hydroxyapatite (HA) prototypes for bone tissue scaffolds are built from Image-Based Design files, featuring an interior architecture of void passages. The results are compared to the HA scaffolds from the Indirect Stereolithography method. Preliminary animal test results will be presented. Piezoelectric ceramic sensors are also built from PZT with the same technique. Direct inkjet printing of ceramics deposits aqueous ceramic slurries in a drop-on-demand fashion. The high temperature flow behavior, droplet formation and the drying behavior of the slurry droplets are studied.

2:45 PM Y4.5
AUTOMATED FABRICATION OF CERAMIC ELECTRONIC PACKAGES BY STEREO-PHOTOLITHOGRAPHY.
Walter Zimbeck, TA&T, Inc., Annapolis, MD; J.H. Jang, W. Schulze, NYSCC, Alfred University, Alfred, NY; R.W. Rice, Consultant, Springfield, VA.

Significant cost and time savings can be realized by applying automated freeform fabrication techniques to the fabrication of ceramic electronic packaging. The widely used thick film/screen printing approach for ceramic packaging involves multiple separate processing stations to build up a multilayer package with embedded electrical connectivity. The current process steps include tape casting, conductor pattern screen printing, punching/filling of vias, dicing, alignment and lamination. The development of low and high temperature co-fire ceramic systems (LTCC and HTCC) has streamlined the firing process, but significant inefficiencies remain in constructing the green state package, such that prototyping of ceramic packages is often very expensive with substantial lead times. This paper describes an integrated approach which combines the automated three dimensional capabilities of stereolithography of ceramics and metals with the high resolution and precision of advanced photolithography systems. The process utilizes photocureable resins filled with sinterable ceramic and metal particles which are applied layer-by-layer and photopatterned to build up a multilayer package. Materials development has focused on a glass-ceramic dielectric, a silver conductor and a barium titanate dielectric. Resin rheology and photocuring characteristics, thermal processing and sintered properties of the materials are described. A breadboard processing system was constructed and the results of fabricating test circuits are presented.

3:30 PM Y4.6
USING LAYERED MANUFACTURING TO CREATE TEXTURED MICROSTRUCTURES IN Si_3N_4 CERAMICS. S. Rangarajan, B.L. Harper A. Safari and S.C. Danforth, Rutgers University, Piscataway, NJ; C. Gasdaska, AlliedSignal Research and Technology, Morristown, NJ.

In the recent years, seeding has been shown to be an effective method to create designer microstructures in Si_3N_4, Al_2O_3 and PZT ceramics. The objective of this research is to create anisotropic and textured Si_3N_4 parts using the Fused Deposition of Ceramics (FDC) process. The FDC process is a layered manufacturing technique, which involves hot extrusion of ceramic particle loaded binders through a small orifice or nozzle. This technique is currently being developed to fabricate high performance structural Si_3N_4 based components. In order to create the textured microstructures, rod-like β -Si_3N_4 seed particles are introduced into the FDC feedstock filaments and done properly, the β -Si_3N_4 seeds will align during extrusion and layering. The β -Si_3N_4 seed particles orient along flow direction due to shear stress gradients induced during filament extrusion and fused deposition. Texture develops in the microstructure during sintering if the re-precipitated β -Si_3N_4 grows preferentially on previously aligned β -Si_3N_4 seeds. In this study, anisometric β - Si_3N_4 seeds were introduced into the starting α - Si_3N_4 powder (AlliedSignal's GS44 grade) at 2.5 and 10 vol.% levels. The effects of the seeds (aspect ratio $\sim$ 4) on the viscosity and resultant microstructure were evaluated using capillary rheology, scanning electron microscopy and x-ray diffraction. It is observed here that the seeds do align during filament extrusion and a significant texture has been detected by x-ray diffraction.

3:45 PM Y4.7
ROBOCASTING AND MECHANICAL TESTING OF AQUEOUS SILICON NITRIDE SLURRIES. G.P. He and D.A. Hirschfeld, New Mexico Tech, Socorro, NM; J. Cesarano III and J.N. Stuecker, Sandia National Labs, Albuquerque, NM.

Aqueous slurries of silicon nitride were freeform fabricated through a novel technique termed robocasting. The process utilizes high solids loading slurries within 10% of green density while using no binder and less than 2 wt% organics in the form of polyelectrolyte dispersants. The combined effects of polyelectrolyte, pH, and solids loading were optimized to produce slurries with suitable rheology for the robo-casting process. Through the layer-wise process, silicon nitride ceramic parts were fabricated without molds and subsequently fired to $>$98% theoretical density. Four point bend testing yielded an average strength of $>$725 MPa using ASTM standard C-1161.
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin company, for the U.S. Department of Energy under contract number DE-AC04-94AL85000.

4:00 PM Y4.8
μMOLD SHAPE DEPOSITION MANUFACTURING OF CERAMIC PARTS. Seowoo Nam, Hao-Chih Liu, Jurgen Stampfl, Fritz B. Prinz, Stanford University, Rapid Prototyping Lab, Stanford, CA.

μMold Shape Deposition Manufacturing (μMoldSDM) is being developed to fabricate complex shaped parts in the millimeter and submillimeter range out of a variety of materials. For this work we present parts made out of ceramics (silicon nitride and alumina) which have been molded (using gelcasting) into wax molds or lithographically patterned photoresist molds. Due to the small size of the parts, conventional post-treatment methods to improve the mechanical properties (grinding etc.) of the sintered parts cannot be used. The as sintered properties of those materials are therefore crucial for the functionality of the parts which are used for gas turbine engines. Depending on the size and the geometry of the part the molds are either manufactured by CNC machining of wax or by deep lithography of photoresist (SU-8). After casting and gelling the mold is removed thermally. The green parts can then be treated in a conventional way. The mechanical and microstructural poperties as well as the geometrical accuracy of the final parts are presented in this work.

4:15 PM Y4.9
AN ANALYSIS OF EXTRUSION IN THE FUSED DEPOSITION OF CERAMICS PROCESS. S. Rangarajan, N. Venkataraman, B.L. Harper, A. Safari and S.C. Danforth, Rutgers University, Piscataway, NJ.

The Fused Deposition of Ceramics (FDC) process is a solid freeform manufacturing technique in which the material deposition process involves the hot extrusion of ceramic particle loaded binders through a small orifice or nozzle. The fully automated FDC process requires ceramic loaded thermoplastic binder, in the form of 1.78 $\pm$ 0.25 mm filaments. The broad objective of this research is to quantify the extrusion pressure as a function of the materials rheological properties, the geometry of the FDC hardware (nozzles etc.) and the flow rate in the FDC process so that material flow during FDC can be precisely controlled. Filament with 55 vol. % of AlliedSignals GS-44 Si_3N_4 in RU9 binder was the principal material for this study. Using a capillary rheometer and dynamic strain rheometer, the steady state, dynamic and transient rheological behavior of the material was evaluated. Using the capillary extrusion process, the pressure drop (ΔP) across dies of various geometries, including FDC nozzles, has been measured. Based on these results, it was determined that the shear behavior of the material at the die entry is crucial, and contributes to ~75% of the overall pressure drop in the FDC process. Finite element modeling (Polyflow^{TM}) has also been used to predict this pressure drop as a function of flow rate and nozzle geometry. Extensional flow behavior of RU955 material was modeled numerically to explain the large die-entry contribution to the pressure drop. Results from these studies and the relationship between the rheological properties such as, yield stress, shear rate exponents, etc. to the pressure drop will be discussed.

4:30 PM Y4.10
LAYER DEPOSITION IN SLURRY-BASED THREE DIMENSIONAL PRINTING. Emanuel Sachs, Patrick Saxton, Bjorn DeBear, Benjamin Polito, Massachusetts Institute of Technology, Department of Mechanical Engineering, Cambridge, MA; Michael Cima, Massachusetts Institute of Technology, Department of Materials Science, Cambridge, MA.

Three Dimensional Printing, an SFF process, can be applied to the fabrication of fine ceramic components by repetitively depositing a slurry of fine ceramic powder, drying a layer, and printing a binder into the layer to define the component. The green part is removed from the powder bed by re-dispersing the powder in the un-printed region. This work develops a new method for depositing the layers of slurry in which a jet of slurry is raster-scanned over the surface of the powder bed with successive lines of slurry deposited rapidly enough (10 Hertz) so that each new line of slurry is deposited before the previous line has slip cast fully. In this manner, a front of liquid slurry is caused to advance over the powder bed at a well-controlled rate and thickness. The merging of successive lines of wet slurry provides a smooth top surface and avoids the formation of defects between scan lines, problems that were associated with previous work where successive lines of slurry where deposited with significant time delay. This paper will present the reasoning and observations which motivated the current approach, develop an order of magnitude model for mapping the slurry deposition process, compare this model to data, present microstructures of powder beds deposited by this technique and compare them to microstructures created by slower speed rastering. The special equipment developed to accomplish the high speed scanning will be briefly reviewed.

4:45 PM Y4.11
THE INFLUENCE OF THE BINDER SYSTEM ON RESOLUTION AND SURFACE FINISH IN THREE DIMENSIONAL PRINTING. Richard K. Holman, Scott A. Uhland, Sherry L. Morissette, Michael J. Cima, Massachusetts Inst of Technology, Dept of Materials Science and Engineering, Cambridge, MA; Emanuel Sachs, Massachusetts Inst of Technology, Dept of Mechanical Engineering, Cambridge, MA.

Three Dimensional Printing, or 3DP(TM), is a solid freeform fabrication (SFF) technique developed at MIT. In Ceramics 3DP(TM) a layer 30 to 100 microns thick is deposited by rastering a jet of ceramic slurry across a substrate. This slurry layer slip casts and is dried to form a cohesive powder bed layer. Next, a digital cross section of the component (extracted from a 3D solid CAD model) is sent to the control software, and a two dimensional image of the component's cross section is ink jet printed with binder solution into the powder bed layer, thus defining the part. The next layer is then deposited and printed, etc. until the entire component has been constructed. This type of forming technique allows for essentially any level of complexity, limited only by the resolution of the printing process and the layer height in the build direction. The size and shape of the primary building block, or binder primitive, are largely determined by the characteristics of the binder solution and the binder deposition process. The structure of the primitive is in turn critical in determining the resolution and surface finish possible with the 3DP(TM) process. Studies are underway to characterize which processes and properties are the controlling factors in defining the primitive size and shape. This work involves droplet impact, post-impact phenomena, and droplet infiltration. Key variables include binder solution viscosity, surface tension, contact angle, droplet size, and droplet velocity.

SESSION Y5: CERAMICS AND SOLUTION PROCESSES
Chairs: Joseph Cesarano and Stephen C. Danforth
Wednesday Morning, April 26, 2000
Salon 13 (Marriott)

8:30 AM Y5.1
INTELLIGENT CAD SYSTEM FOR MULTI-MATERIAL LM PROCESS. Dan Qiu, GuoHua Wu, Kate Higgins, Noshir A. Langrana, Mechanical and Aerospace Engineering, Piscataway, NJ; Stephen C. Danforth, Ahmad Safari, Ceramic and Materials Engineering, Piscataway, NJ; Mohsen Jafari, Industrial Engr, Piscataway, NJ.

The multi-material Layered Manufacturing (LM) technology is under development in recent years. One of the main concerns of LM technologies is quality of the part, specifically, to keep the voids and defects within the acceptable limits. For multi-material LM, there are additional issues about materials matching within one part at the interface boundaries. Our ongoing research on multi-material layered manufacturing, the material-based build characteristics are defined. The hardware (called MURI Machine) is designed to accommodate this requirement. To fabricate high quality part's, and to make the development generic yet compatible with our hardware, an in-house virtual simulation system and an intelligent multi-material toolpath generation system have been developed. The multi-material toolpath generation software uses slice file as input data. This system includes issues such as intelligent toolpath features for void elimination, and intelligent toolpath features for machine control. After the multi-material toolpath file generated by the in house software, the existing virtual graphical simulation as well as well selected part fabrication experiments are being used to validate it. The virtual simulation utilizes physical roadshapes captured using video microscopy method. Problems of voids and defects, interface mismatch between adjacent materials are readily detected and quantified in the virtual simulation results. The parts have been fabricated using different materials including wax, PZT, silicone nitride and 17-4PH stainless steel powder. Several objects with complex concave contours have been successfully simulated. The components such as metal molds, turbine blades, actuators, and fixtures have been designed, simulated and fabricated. The properties of parts are being quantified in terms of quality and accuracy.

8:45 AM Y5.2
ROBOCASTING OF MULTI-MATERIAL SYSTEMS: MULLITE-ZIRCONIA. Hugh B Denham, John N. Stuecker, Joseph Cesarano III, Sandia National Labs, Albuquerque, NM.

Robocasting is a technique for fabrication of three-dimensional parts by a layerwise process. Aqueous slurries of ceramic powders were used to create unique parts consisting of more than one material. Zirconium oxide (zirconia) can be combined with mullite (alumino-silicate) to provide toughening. The thermal expansion mismatch between zirconia and mullite was used, along with discrete placement of each component provided by robocasting, yielding parts with surfaces in compression after sintering. Efforts toward adapting this multiple material system for robocasting, slurry development along with computer modeling support, will be discussed. Finally, the mechanical behavior of unique zirconia-mullite composites will be discussed, along with the potentials for graded structures and other multiple material systems.
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

9:00 AM Y5.3
FREEFORM FABRICATION OF MULTIMATERIAL STRUCTURES. Haripin Chandra, Sridhar Kasichainula and Paul Calvert, Arizona Materials Labs., Tucson AZ.

Layerwise processing methods allow different materials to be combined into a single monolithic solid. Two examples will be presented. Bars of epoxy resin, with a glass fiber screen reinforcement between one or more layers, have been made by extrusion freeform fabrication and the mechanical properties measured in bending. It is found that the fracture toughness is greatly increased if the reinforcing layer is weakly bonded into the composite and if multiple layers of reinforcement allow extensive pullout behind the crack front. The results will be compared with models for the fracture process. Glass ceramic bars have also been freeformed with cofired silver between layers. The morphology, conductivity and mechanical properties of these will also be reported. It is hoped that these results will shed light on the role of layered structures in toughening bone and mollusc shells.

9:15 AM *Y5.4
FREEFORM FABRICATION OF CERAMICS BY HOT MELT INK-JET PRINTING. B. Derby, N. Reis, Manchester Materials Science Centre, UMIST, Mancghester, UNITED KINGDOM; K. Seerden, P.S. Grant, Department of Materials, University of Oxford, Oxford, UNITED KINGDOM; J.R.G. Evans Department of Materials Engineering, Queen Mary and Westfield College, London, UNITED KINGDOM.

Ink-jet printing is a versatile freeform fabrication technique with a high spatial resolution. By suspending ceramic particles in low melting point organic materials and printing above the melting point, rapid cooling on impact after printing results in rapid layer growth. Current results from a collaborative programme studying the hot wax ink-jet printing of structural ceramic components will be reported.

Similarities and key differences with related fabrication methods will be reviewed and key points for future research and development discussed.

9:45 AM Y5.5
PROCESS-PROPERTY-PERFORMANCE RELATIONSHIPS FOR FUSED DEPOSITION OF CERAMICS (FDC) FEEDSTOCK MATERIALS. N. Venkataraman, S. Rangarajan, B. Harper, M.J. Matthewson, A. Safari and S.C. Danforth, Department of Ceramic and Materials Engineering, Rutgers University, NJ.

Fused deposition of ceramics (FDC) is an extrusion based layered manufacturing process. It uses a high solids loaded (>50 vol. % ceramic or metal powder) thermoplastic binder in filament form as the feedstock material. The filament acts as both the piston driving the extrusion process and the feedstock material being deposited in the X-Y direction onto a Z-stage platform. The primary mode of failure of the filament during the FDC process is via buckling. This work has shown that the compressive modulus and the apparent viscosity of the feedstock materials determine their buckling behavior. A materials selection map has been developed, based on the ratio of filament elastic modulus to the apparent viscosity. In addition, the actual pressure needed to drive the extrusion through FDC nozzles has been determined as a function of nozzle geometry, flow rate and solids loading. A process map indicating the process performance of the feedstock materials has been developed based on the filament elastic modulus and the measured pressure drop. The paper will discuss the salient features of the material selection map and the process map. In addition, efforts to understand the effect of processing variables such as solids loading, extrusion conditions, particle characteristics and agglomeration on the critical mechanical and rheological properties of the feedstock material will be discussed.
This work was sponsored under the ONR-MURI contract N00014-96-1-1175.

10:15 AM Y5.6
TAILORING SUSPENSION CHEMISTRY FOR FABRICATION OF DEFECT-FREE POWDER BEDS VIA SLURRY-BASED THREE-DIMENSIONAL PRINTING (3DP^{TM}). S.L. Morissette, S. Uhland, R. Holman, M. Cima, E. Sachs, Ceramics Processing Research Laboratory, Massachusetts Institute of Technology, Cambridge, MA.

Suspension composition determines several parameters critical to the slurry-based three-dimensional printing (3DP^{TM}) process, including slip casting rate, powder bed density and surface topography. Thus, fabrication of high quality, complex-shaped ceramic components via 3DP^{TM} requires careful control over slurry chemistry and printing conditions. Current efforts focus on investigating the influence of composition (i.e., dispersant type and concentration, solvent composition, solids volume fraction) on suspension stability and the resulting powder bed density, interactions between the as-deposited slurry and powder bed, surface topography, and defect generation. For example, recent studies have shown that structural and inter-layer defects (e.g., density gradients and slurry migration) resulting from differential slip casting (DCS) can be eliminated by varying binder content and solvent chemistry. The origin of inter-layer defects (i.e., air/bubble entrapment) generated at the slurry-powder bed interface remains unclear. This presentation discusses the key 3DP^{TM} process phenomena and the approaches used to tailor printing suspensions for improved printing behavior.

10:30 AM Y5.7
PART RETRIEVAL IN THE SLURRY-BASED 3DP PROCESS. Scott A. Uhland, Richard K. Holman, Sherry L. Morissette, Michael J. Cima, Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA; Emanuel M. Sachs, Massachusetts Institute of Technology, Department of Mechanical Engineering, Cambridge, MA.

Products which incorporate ceramic components frequently demand properties and shapes that challenge contemporary forming techniques. The Three-Dimensional Printing (3DP) process has been modified to incorporate colloidal science for the fabrication of fine ceramic parts. Dielectric components were built using a sequential layering process of a ceramic powder bed followed by ink jet printing of a binder. An important processing step in 3DP is removing the printed components from the powder bed. The part retrieval process plays a key role in the resulting shape and properties of the ceramic parts. Part retrieval is achieved through the redispersion of the powder bed. The addition of a redispersant to the slurry, e.g., polyethylene glycol, enables the redispersion of the ceramic powder bed. Processing conditions, i.e. powder bed chemistry and the chemistry of the redispersing liquid, must be controlled throughout the process due to their strong influence the redispersion behavior of the powder bed. The processing technology has been used for the fabrication of dielectric RF components with extremely tight dimensional tolerances.

10:45 AM *Y5.8
GAS PHASE SOLID FREEFORM FABRICATION. Harris L. Marcus, Shay Harrison, James E. Crocker, Lianchao Sun, Eric Geiss and Leon Shaw, Institute of Maaterials Science, Metallurgy and Materials Engineering Department, Storrs, CT.

Localized CVD is the basis of two approaches to Solid Freeform Fabrication and related technologies. This paper will describe the recent efforts in selective area laser deposition (SALD) and SALD vapor infiltration (SALDVI). The SALD materials to be reported on include CVD of SiC, C, and Si3N4. The SALDVI process localized CVD into powders of SiC, Si3N4, Ni, and Mo. The resulting microstructures will be defined as a function of the processing parameters and the chemical interactions between the CVD materials and the powders.

11:15 AM Y5.9
EXPERIMENT AND MODELING ON PHYSICAL/CHEMICAL LIQUID DEPOSITION BASED SOLID FREEFORM FABRICATION. Gongyao J. Zhou and Zongyan He, Drexel University, Dept. of Mechanical Engineering and Mechanics, Philadelphia, PA.

Physical/Chemical Liquid Deposition Based Solid Freeform Fabrication (P/CLD-SFF) is a new rapid tooling (RT) technique proposed by the authors. It is based on the following experimental fact. When cold (room temperature) solution or liquid reactant is sprayed from a nozzle and contacted with a hot substrate, it can evaporate or decompose or react each other (if there are two or more reactants are sprayed at the same time), then the solid solute or resultant will deposit on the substrate. By controlling the motion of the nozzle and the spray time, a desired 3-D shape of deposited material can be formed through layer by layer scanning. The proposed P/CLD-SFF includes Physical Liquid Deposition-SFF (PLD-SFF) and Chemical Liquid Deposition-SFF (CLD-SFF). Although having different deposition principles, the two techniques have very similar technical processes and can be carried out with a same P/CLD-SFF system, only changing the starting materials. Compared with other RT techniques (Jakubenas, Sanchez, and Marcus, 1997), P/CLD SFF has higher accuracy and deposition rate, lower cost and investment. Especially, a wide range of materials such as salts, metals, alloys, ceramics and carbon materials can be deposited by P/CLD-SFF to form desired patterns or parts, and their chemical compositions, density and other properties can be controlled by designing suitable technical parameters.
Through a series of experiments, the authors found that the microstructure and strength of the deposited solid and the accuracy of the products all depend on the deposition temperature, liquid's flow rate and moving velocity of the nozzle. In order to calculate deposition rate, determine the above technical parameters and explain deposition phenomena, the authors proposed the heterogeneous nuclear and growth models on the separating process of solute from solution. Based on these models, a deposition dynamic model was deduced to describe the dynamic characteristics of PLD-SFF. The calculation results of the models were compared with experiments and used to optimize technical parameters. Some deposition phenomena were analyzed and discussed based on these results.
1. P. Jacobs, Stereolithography and Other RP&M Technologies, published by SME, USA, 1996

11:30 AM Y5.10
SILICON DIOXIDE NANOTUBES PREPARED BY ANODIC ALUMINA AS TEMPLATES. Ming Zhang, Y. Bando, National Institute for Research in Inorganic Materials, Tsukuba, JAPAN.

Recently based on an laser ablation and catalytic chemical reaction methods, large-scale synthesis of silica nanowires with ~40nm of diameter were prepared. Unfortunately, these techniques are difficult to be used for preparing silica nanotubes. In this paper, the aligned silicon dioxide nanotubes with diameter of 30~40nm synthesized by the sol-gel template method are presented. This process involves the growth of nanotubes from the ordered nanochannel-array pores in anodic alumina. For a silica sol aged at room temperature and dipped for 1min., nanowires have been formed in a shorter period of aging time (2 days); and nanotubes connecting with solid nanofibers have been obtained in a longer aging time (30 days). The formation of nanotubes depends strongly on the temperature of the sol. For a short dipping time (<1min.), the bamboo-like nanofibers were prepared when the sol was at high temperature (323K); however, the perfect nanotubes with the sharp wall were synthesized for the lower sol temperature (278K). The lower sol temperature is, the more smooth the inside wall of nanotubes is. It is proved that the viscosity plays an important role on the morphology of nanotubes.

11:45 AM Y5.11
DIRECT FABRICATION OF $BaTiO_3/SrTiO_3$ LAYERED FILMS BY HYDROTHERMAL/ELECTROCHEMICAL METHOD IN A FLOW CELL. Tomoaki Watanabe, Wojciech Suchanek, Naoki Kumagai and Masahiro Yoshimura, Tokyo Institute of Technology, Materials and Structures Laboratory, Yokohama, JAPAN.

Processing of thin films in the high-tech integrated devices has been dominated by physical vapor deposition (PVD) and chemical vapor deposition (CVD). In spite of many undoubted advantages of these processing routes, they usually require relatively high temperatures (above 500°C). Additionally the PVD techniques require complicated equipment, such as high-vacuum systems, plasma systems, etc. The CVD processing utilizes typically gases, which are toxic, flammable, and/or corrosive, moreover some of them, such as silane, may even explode, therefore they present a serious hazard to humans. These features make the CVD and PVD environmentally stressed and expensive. However, it is also possible to fabricate the thin films directly from the solution under almost ambient conditions, for example by hydrothermal and/or electrochemical methods. Solution processing gives in many cases similar results than other processing such as CVD, PVD but consumes less energy, is environmentally friendly, requires simple equipment, and is inexpensive. We have proposed "Soft Solution Processing" for those methods. In this report, layered thin films in the $BaTiO_3 - SrTiO_3$ system have been fabricated by a hydrothermal-electrochemical method either in a closed autoclave or in a flow system using the titanium substrate and Ba- and Sr-hydroxides or acetates as sources of titanium, barium, and strontium, respectively. The synthesis conditions (temperature in the range of 120-200°C, current density of 1-20mA/cm^2, flow rates of 1-50 cm^3/min, duration of 1-24 h) allowed an easy control of the microstructure of the titanate layers. The multilayered $BaTiO_3 - SrTiO_3$ thin films have been revealed by XRD, AFM, and XPS at various stages of their preparation. Based upon the experimental results, a growth mechanism of the $BaTiO_3 - SrTiO_3$ double layers has been proposed. We are also developing of in situ patterning of $BaTiO_3$ and $SrTiO_3$ films.